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6. AUTHOR(S) Dr Robert M. Metzger					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dept of Chemistry University of Alabama LLoyd Hall, Box 870336 Tuscaloosa AL 35487-0336					
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 110 Duncan Ave Room B115 Bolling AFB DC 20332-8080 Dr Charles Y-C. Lee				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
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13. ABSTRACT (Maximum 200 words) The synthetic chemistry of dithiadiazafulvalenes (DTDAF) was studied in detail: these one and two-electron donors, ore powerful than the well-known tetrathiafulvalenes (TTF, 1), but more chemically more tractable than the unstable tetraazafulvalenes, are a significant departure from ordinary organic donors, and therefore show promise in the search for new organic superconductors. A 2:5 complex of diphenyl-diacetyldithiadiazafulvalene (o2Ac2DTDAF, 4c) with the electron acceptor tetracyanoquinodimethan (TCNQ, 11a), including one molecule of acetonitrile, the solvent of crystallization (CH3CN), provided room-temperature conductivity $\sigma=0.011$ S/cm (Siemens per centimeter). An unusual diamagnetic flux exclusion signal (for 5 per cent of the sample at 4.4 Kelvin) was determined to be an artifact due to a ferromagnetic impurity. A TCNQ complex of dimethyltetracetyldTDAF, 4b had $\sigma=0.083$ S/cm at room temperature. A new acceptor, dioxotetracyanobisindanedione vinylidene (DOTCBIV), 5, provided a complex with TTF with $\sigma=0.6$ S/cm at room temperature. Many complexes wity fullerene, C60 (12), were made, but were electrically insulating. Studies of Langmuir-Blodgett films of potassium-doped C60 (monolayers on polyethylene terephthalate) may help to determine the boundary between 2-D and 3-D superconductivity.					
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THE UNIVERSITY OF ALABAMA
College of Arts and Sciences

DEPARTMENT OF CHEMISTRY

Laboratory of Molecular Electronics
Tel 1-(205)-348-5952
Fax 1-(205)-348-9104
email=rmetzger @ ua1vm.ua.edu

February 12, 1997

Dr. Harold Weinstock
Physics and Electronics
Air Force Office of Scientific Research (AFMC)
Bolling Air Force Base
Washington, DC 20332-0001

Dr. Charles Y. C. Lee
Chemistry & Materials Science
Air Force Office of Scientific Research
Bolling Air Force Base
Washington, DC 20332-6448

Dear Drs. Weinstock and Lee:

Enclosed please find nine copies (sent to Dr. Lee) plus one copy (to Dr. Weinstock) of the Final Report for AFOSR Contract F-49620-92-J-0529 (Organic and Polymeric Superconductors). Thank you very much for your past support.

Robert M. Metzger
Professor

cc: Dr. Robert Wells, Assistant Vice President for Research
Pam Standifer, Contracts and Grants Accounting

Final Report to Air Force Office of Scientific Research

Date: February 12, 1997

Period 1 October 1992 - 1 March 1996

Grant Title: Organic and Polymeric Superconductors

AFOSR Grant No. F-49620-92-J-0529

Principal Investigator: Robert M. Metzger

Co-Investigator: Michael P. Cava

Institution: Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487-0336

Cognizant AFOSR Program Managers: Charles Y.C. Lee and Harold Weinstock

Abstract

The synthetic chemistry of dithiadiazafulvalenes (DTDAF) was studied in detail: these one and two-electron donors, more powerful than the well-known tetrathiafulvalenes (TTF, **1**), but more chemically more tractable than the unstable tetraazafulvalenes, are a significant departure from ordinary organic donors, and therefore show promise in the search for new organic superconductors. A 2:5 complex of diphenyldiacetyldithiadiazafulvalene ($\phi_2\text{Ac}_2\text{DTDAF}$, **4c**) with the electron acceptor tetracyanoquinodimethan (TCNQ, **11a**), including one molecule of acetonitrile, the solvent of crystallization (CH_3CN), provided room-temperature conductivity $\sigma=0.011$ S/cm (Siemens per centimeter). An unusual diamagnetic flux exclusion signal (for 5 per cent of the sample at 4.4 Kelvin) was determined to be an artifact due to a ferromagnetic impurity.

A TCNQ complex of dimethyltetracetyldTDAF, **4b** had $\sigma=0.083$ S/cm at room temperature. A new acceptor, dioxotetracyanobisindanedione vinylidene (DOTCBIV), **5**, provided a complex with TTF with $\sigma=0.6$ S/cm at room temperature. Many complexes with fullerene, C_{60} (**12**), were made, but were electrically insulating.

Studies of Langmuir-Blodgett films of potassium-doped C_{60} (monolayers on polyethylene terephthalate) may help to determine the boundary between 2-D and 3-D superconductivity.

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1. Dithiadiazafulvalenes - New Strong Electron Donors.

As a novel variation on tetrathiafulvalene (TTF) **1**, its selenium and tellurium analogs, and their derivatives, we prepared new donors (dithiadiazafulvalenes, DTDAFs) **4a**, **4b**, **4c**, and **4d**; their electrochemistry (Table I) shows them to be powerful new donors.

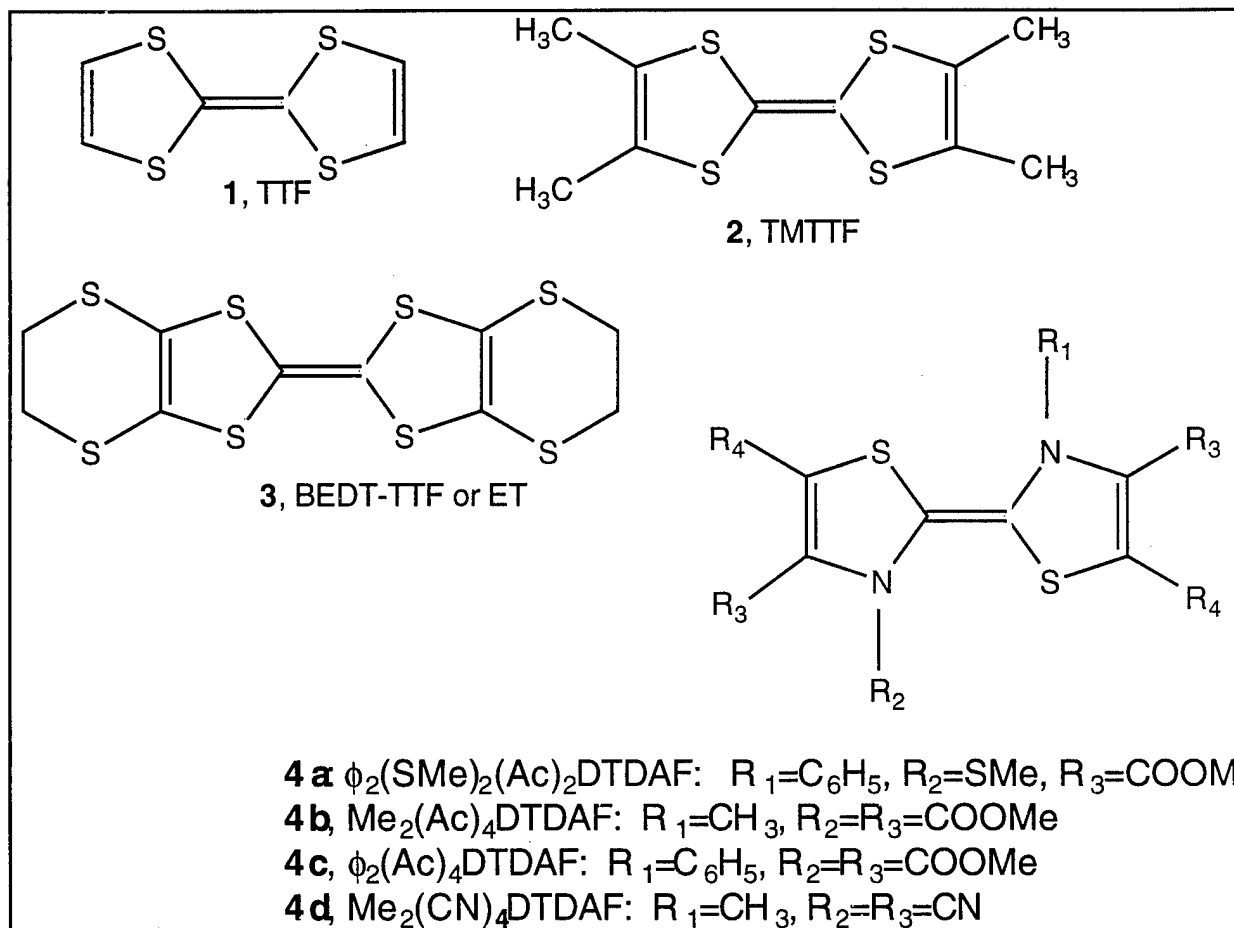


Table I. Oxidation potentials of TTF (1), TMTTF (2), and BEDT TTF (3) and of the novel DTDAFs **4a**, **4b**, **4c**, and **4d**, determined by cyclic voltammetry (V vs. SCE).

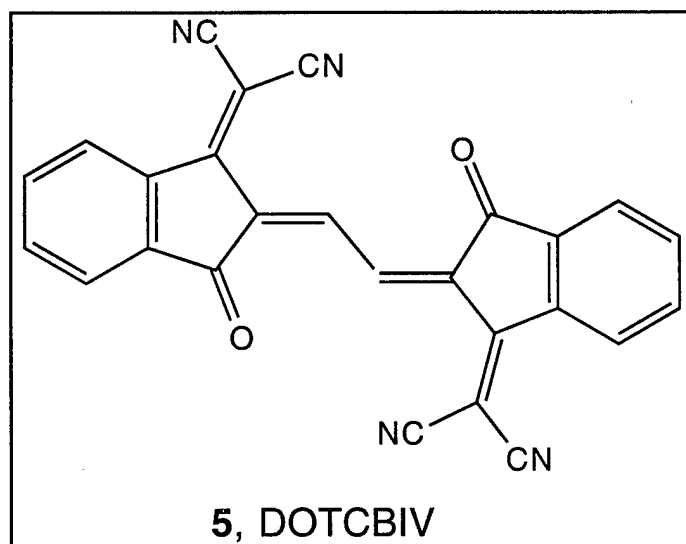
Compound	E^1_{ox} , V	E^2_{ox} , V	$E^2_{ox} - E^1_{ox}$, V
TTF (1)	0.35 [13]	0.71 [13]	0.36 [13]
TMTTF (2)	0.29 [13]	0.65 [13]	0.36 [13]
ET (3)	0.58	1.00	0.42
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$, 4a	0.00	0.48	0.48
$\text{Me}_2\text{Ac}_4\text{DTDAF}$ 4b	0.02	0.26	0.24
$\phi_2\text{Ac}_4\text{DTDAF}$, 4c	0.15	0.66	0.51
$\text{Me}_2(\text{CN})_4\text{DTDAF}$, 4d	0.42	0.63	0.21

In complexes with the electron acceptor TCNQ, they yielded new semiconductors (Table 2) but no new metals.

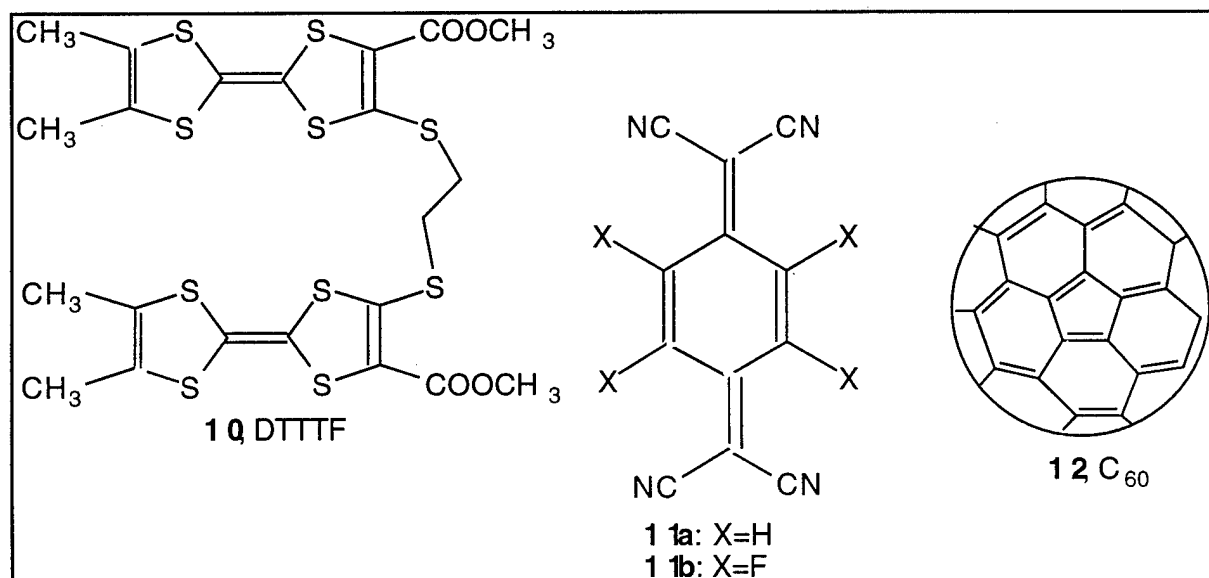
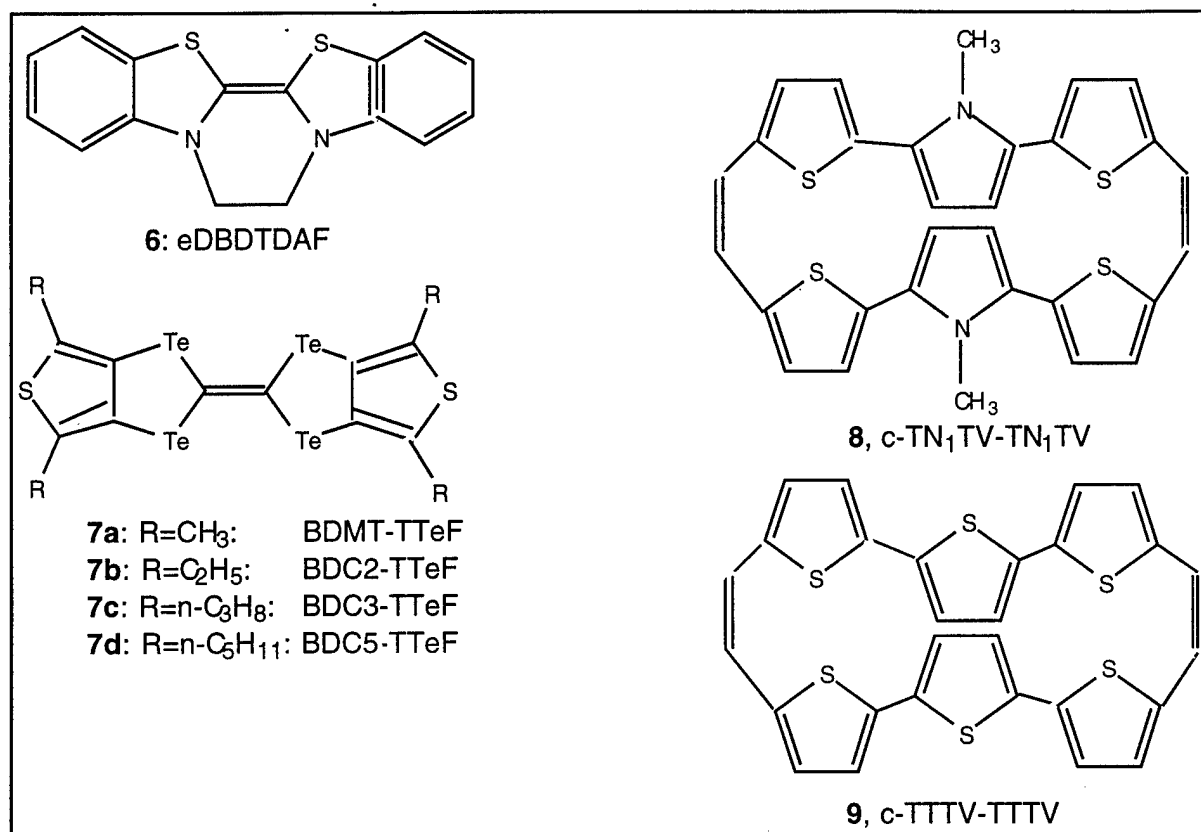
Table 2. Room temperature conductivities of complexes of **4a**, **4b**, **c** with TCNQ (standard 2-probe method, compaction, gold wire, gold paste).

Donor	Acceptor	Ratio	Conductivity (300 K) σ , S cm^{-1}
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$, 4a	TCNQ	1:1	1.6×10^{-7}
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$, 4a	TCNQ	1:4 (+ 2 CH_3CN)	1.1×10^{-7}
$\text{Me}_2\text{Ac}_4\text{DTDAF}$ 4b	TCNQ	1:4	8.3×10^{-2}
$\phi_2\text{Ac}_4\text{DTDAF}$, 4c	TCNQ	1:1	10^{-10}
$\phi_2\text{Ac}_4\text{DTDAF}$, 4c	TCNQ	2:5	1.1×10^{-2}

2. New Electron Acceptor



A new one-electron acceptor, dioxotetracyanobisindanedione vinylidene DOTCBIV, **5** is a strong electron acceptor, with two quasi-reversible electrochemical reduction waves ($E^1_{red} = 0.05$, $E^2_{red} = -0.11$; $E^1_{ox} = -0.06$, $E^2_{ox} = 0.11\text{V}$ vs SCE, in acetonitrile). It reacts with TTF and TMTTF to form charge-transfer complexes, whose room-temperature conductivities (2-probe method, compaction, gold wire, gold paste) are 1.7 and 0.01 S/cm respectively. An effort to prepare the octacyano derivative of BIV was not successful.



3. Physical Measurements.

The Langmuir-Blodgett films of C₆₀ [1,2] form monolayers only from very dilute dropping solutions (0.05 mg/mL), and then give areas of about 96 Å²/molecule, i.e. a true monolayer forms [3]. When doped with K, a 50 monolayer sample of C₆₀ shows a low-field signal, measured in an EPR spectrometer, with hysteresis, at or below 8.1 K: this is a sensitive test of the Meissner effect for some unknown fraction of the sample, due to the formation of K₃C₆₀ within the LB multilayer: **the world's first superconducting Langmuir-Blodgett film** [4-

6]. When more K is added, the signal disappears (formation of insulating K_6C_{60}) [4,5]. A new study of the superconductivity of K_3C_{60} LB films finds slightly higher critical temperatures [13].

The physical results for many of the complexes described in Table 3 have been published [6-9]. Overall, three are promising conductors: $(4b)_2(TCNQ)_5CH_3CN$, $4a+TCNQ$, $1+25a$. The crystal structure of the 1:5 complex of **7** with **32a** has been determined by Robert and co-workers: the neutral and anionic TCNQ species form a segregated stack, while the DTDAF cations do not overlap with each other: this is a classic "mixed" TCNQ stack structure, with expected semiconductive properties. By crystal structure analysis, $(4b)_2(TCNQ)_5CH_3CN$ forms a similar structure, with good TCNQ stacks, but where the phenyl rings on DTDAF **4b** prevent efficient stacking of the DTDAF moieties.

Table 3. List of complexes and their conductivities.

Donor	Acceptor	Solvent	Stoich.	Size, mm	Phys. Properties
$\phi_2(SMe)_2Ac_2DTDAF$, 4a	TCNQ, 11a	CH ₃ CN	1:1	powder	black $\sigma=1.6 \times 10^{-7}$ S/cm
	TCNQ, 11a	CH ₃ CN	1:4+2	CH ₃ CN	black powder $\sigma=1.12 \times 10^{-7}$ S/cm
Me ₂ Ac ₄ DTDAF, 4b	TCNQ, 11a	CH ₃ CN	1:4	powder	black powder $\sigma=8.3 \times 10^{-2}$ S/cm
ϕ_2Ac_4DTDAF , 4c	TCNQ, 11a	(CH ₂ Cl) ₂ +CH ₃ CN	2:5	1.0×0.4×0.07	black plate, $\sigma=0.011$ S/cm [9]
		CH ₂ Cl ₂	1:1	1.1×1.0×0.1	black plate, $\sigma < 10^{-10}$ S/cm [9], polycrystalline
	TCNQF ₄ , 11b	CH ₃ CN C ₆ H ₅ Cl+CH ₂ Cl ₂	1:2 1:x	small 1.6×1.1×0.01	black tiny plate black polycryst. [9] plate $\sigma=1.2 \times 10^{-6}$ S/cm
	C ₆₀ , 12	CH ₂ Cl ₂ +CS ₂	1:x	1.5×0.04×0.03	black $\sigma < 10^{-10}$ S/cm [9] twinned
	I ₂	CHCl ₃	1:x	0.8×0.7×0.6	black $\sigma=1.1 \times 10^{-7}$ S/cm OK for X-ray [9]
		C ₂ H ₅ OC ₂ H ₅	1:x	0.5×0.04×0.04	black needle $\sigma < 10^{-10}$ S/cm [9]
eDBDTDAF, 6	TCNQ, 11a		2:1	powder	black, $\sigma < 10^{-10}$ S/cm
TTF, 1	DOTCBIV, 5	CH ₂ Cl ₂ +n-C ₆ H ₁₄	1:x	powder	$\sigma=0.6$ S/cm
BDMT-TTeF, 7a	DOTCBIV, 5	CH ₂ ClCH ₂ Cl+CS ₂	1:x	needle	black, $\sigma < 10^{-10}$ S/cm
BDMT-TTeF, 7a	TCNQ, 11a	CH ₂ ClCH ₂ Cl	1:x		tiny plate
	C ₆₀ , 12	CS ₂	1:x		tiny plate.
		CS ₂	1:1+1	CS ₂	rhombic plate, cryst.str. [6] $\sigma < 10^{-10}$ S/cm [7]
BD2T-TTeF, 7b	C ₆₀ , 12	CS ₂ CH ₂ Cl ₂ +CS ₂	1:x 1:x	 1.0×0.9×0.04	hexagonal plate black polycrystal, $\sigma < 10^{-10}$ S/cm
BD3T-TTeF, 7c	C ₆₀ , 12	CS ₂	1:x	0.8×0.7×0.02	$\sigma < 10^{-10}$ S/cm
BD5T-TTeF, 7d	C ₆₀ , 12	CS ₂	1:x	0.4×0.3×0.02	$\sigma < 10^{-10}$ S/cm
DTTF, 10	C ₆₀ , 12	CS ₂ or C ₆ H ₆	1:x	1.5×0.05×0.04	needle, insulator [9]
c-TTTV-TTTV, 8	TCNQF ₄ , 11b		1:1	powder	$\sigma=9.5 \times 10^{-3}$ S/cm [8]
c-TN ₁ TV-TN ₁ TV, 9	TCNQF ₄ , 11b		1:1	powder	$\sigma=1.2 \times 10^{-4}$ S/cm [8]

The synthetic chemistry of the dithiadiazafulvalenes has been published in full [10]. The criteria for the formation of organic superconductors, and of the limiting conductivity of organic polymers has been published [11]. A new polymeric semiconductor has also been studied [12].

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Dr. Gregory V. Tormos (present employment: Eastman Chemical Co., Batesville, AR)

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None.